Ph.D. Synopsis

Growth, Synthesis, Modification and Characterization of Novel Thin Films for Nanostructure Applications

Abstract:-

Thin film science and technology plays an important role in the development of devices in the future ranging from energy-efficient display devices to energy-harvesting and storage devices such as solar cell, fuel cell, batteries, super capacitor, semiconductor devices, gas sensors etc. Thin films have properties that can be different from that of their corresponding bulk structures. A film is considered as thin, as long as its surface properties are different from its bulk behavior. Thin films have larger surface to volume ratio, hence the surface and near surface characteristics decide the properties of the thin film. As a result thin film properties generally depend on the thickness of the film which extends from few micrometers to nanometer, substrate nature on which the films are grown and deposition methodology/conditions used in the fabrication of thin films. Thin film fabrications are generally carried out by depositing the required material in the atomistic deposition (atom by atom) over the required substrate, which may result in either single crystalline, polycrystalline, or amorphous structure depending on the deposition conditions. Thin film technology has the potential to engineer the various properties such as porosity, surface morphology, surface roughness, and crystallite size. These advantages in thin film assist in the development of new products and minimize the waste as in the conventional manufacturing techniques. This research work provides various thin film processing methods, mechanism behind the growth, important tools used for the characterization of thin films for various applications

1. Introduction

Thin Films field of material science and engineering community's ability to conceive the novel materials with extraordinary combination of chemical, physical and mechanical properties has changed the modern society. There is increasing technological progress. Modern technology requires thin films for different applications. Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films, and scientific curiosity about the behavior of two-dimensional solids has been responsible for the immense interest in the study of science and technology of the thin films. These studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry, and structure of the film. When we consider a very thin film of some substance, we have a situation in which the two surfaces are so close to each other that they can have a decisive influence on the internal physical properties and processes of the substance, which differ, therefore, in a profound way from those of a bulk material. The decrease in distance between the surfaces and their mutual interaction can result in the rise of completely new phenomena. Here the one dimension of the material is reduced to an order of several atomic layers which creates an intermediate system between macro systems and molecular systems, thus it provides us a method of investigation of the microphysical nature of various processes. Thin films are especially appropriate for applications in microelectronics and integrated optics. However the physical properties of the films like electrical resistivity do not substantially differ from the properties of the bulk material. For a thin film the limit of thickness is considered between tenths of nanometer and several micrometers. Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. The properties of material significantly differ when analyzed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optical properties or wear resistance. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter. Thin films are formed mostly by deposition, either physical or chemical methods. Thin films, both crystalline and amorphous, have immense importance in the age of high technology. Few of them are microelectronic devices, magnetic thin films in recording devices, magnetic sensors, Gas sensor, A. R. coating, photoconductors, IR

detectors, Interference filters, Solar cells, polarizer's, Temperature controller in satellite, superconducting films, anticorrosive and decorative coatings.

The vast varieties of thin film materials, their deposition, fabrication techniques, spectroscopic characterization and optical characterization probes are used to produce the devices. It is possible to classify these techniques in two ways. Physical method covers the deposition techniques which depend on the evaporation or ejection of the material from a source, i.e. evaporation or sputtering, whereas chemical methods depend on physical properties. Structure property relationships are the key features of such devices and basis of thin film technologies. Underlying the performance and economics of thin film components are the manufacturing techniques on a specific chemical reaction. Thus chemical reactions may depend on thermal effects, as in vapor phase deposition and thermal growth. However, in all these cases a definite chemical reaction is required to obtain the final film. When one seeks to classify deposition of films by chemical methods, one finds that they can be classified into two classes. The first of these classes is concerned with the chemical formation of the film from medium, and typical methods involved are electroplating, chemical reduction plating and vapor phase deposition. A second class is that of formation of this film from the precursor ingredients e.g. iodization, gaseous iodization, thermal growth, sputtering ion beam implantation, CVD, MOCVD and vacuum evaporation. The methods are often capable of producing films defined as thin films, i.e. 1 μm or less and films defined as thick films, i.e. 1 μm or more. However, there are certain techniques which are only capable of producing thick films and these include screen printing, glazing, electrophoresis deposition, flame spraying and painting.

In the advancement of science and technology the discovery of novel materials those are having varied characteristics and applications have played an important role. Characterization is an important step in the development of exotic materials. The complete characterization of any material consists of phase analysis, compositional characterization, structural elucidation, micro-structural analysis and surface characterization, which have strong bearing on the properties of materials. This has led to the emergence of variety of advanced techniques in the field of materials science. A wide variety of characterization techniques are used to evaluate the material quality of the thin films. The structural properties of the polycrystalline films are studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM) in non-contact mode

while the presence of crystalline phases by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Composition measurements are made by energy dispersive analysis of X-rays (EDAX) equipped with SEM. The electrical properties of the materials are investigated by Four-point probe and Hall Effect measurements. The optical properties of the films are studied using transmission measurements.

2. Review of Literature and Development in the subject (Previous work done in the relevant area):

The scaling down of complementary Metal oxide semiconductor (CMOS) transistors requires replacement of conventional silicon dioxide layer with higher dielectric constant (K) material for gate dielectric. To reduce the gate leakage current and also to maximize gate capacitance high K gate oxide materials are required. In the previous work mixed oxide of $(Ta_2O_5)_x(TiO_2)_{1-x}$ is chosen as alternative to silicon dioxide (SiO_2) and detail study on the electrical properties like capacitance, dielectric constant, fixed charges, interface state density and leakage currents are observed. In our experiment we used P-type single crystal (100) silicon as substrate and DC reactive magnetron sputtering method with combination of Tantalum and Titanium metal targets to deposit thin films. Oxygen is used as reactive gas along with Argon. The thickness of deposited films is in the range of 300+-10 nm with substrate temperature 600^0C.Agilent make 4284 A model L-C-R meter along with Karlsuss wafer probe station is used for C-V measurement and Agilent 4155 is used for I-V measurement.MOS capacitor have been fabricated with aluminum as top electrode to perform bi-directional capacitance –voltage and current-voltage analysis. Dielectric constant (K) and flat band voltage (V_{FB}), fixed charges (Q_f), interface state density (Dit') and equivalent oxide thickness (EOT) are obtained from the bidirectional C-V analysis. A maximum dielectric constant of 34.28 is achieved. The fixed charge for that film is $7.3x10^{11}$ per cm^2.The average interface state density is $2.0x10^{31}$ $cm^{-2}eV^{-1}$ and EOT that we have achieved is 33.8 nm. From I-V analysis the minimum leakage current density achieved is $3.5x10^{-7}$A per cm^2. The breakdown voltage is at 45V corresponding to the field of 1.5 MV per cm.Our aim is to study the electrical properties of mixed oxide $(Ta_2O_5)_x(TiO_2)_{1-x}$ thin film for application as a high K gate dielectric in microelectronic applications. Emphasis is given on the dielectric constant value (K). The maximum dielectric constant (K) we have achieved is in the comparable range for our application.

3. Objectives of Research/ Proposed Hypothesis:

Although the study of thin film phenomena dates back well over a century, it is really only over the last four decades that they have been used to a significant extent in practical situations. The requirement of micro miniaturization made the use of thin and thick films virtually imperative. The development of computer technology led to a requirement for very high density storage techniques and it is this which has stimulated most of the research on the magnetic properties of thin films. Many thin film devices have been developed which have found themselves looking for an application or, perhaps more importantly market. In general these devices have resulted from research into the physical properties of thin films. Secondly, as well as generating ideas for new devices, fundamental research has led to a dramatic improvement in understanding of thin films and surfaces. This in turn has resulted in a greater ability to fabricate devices with predictable, controllable and reproducible properties. The cleanliness and nature of the substrate, the deposition conditions, post deposition heat treatment and passivation are vital process variables in thin film fabrication. Therefore, prior to this improvement in our understanding of thin films, it has not really been possible to apply them to real devices. Thirdly, much of the finance for early thin film research originated from space and defense programs to which the device cost is less important than its lightweight and other advantages, the major applications of thin film technology are not now exclusively in these areas but rather often lie in the domestic sector in which low cost is essential. Thin film materials have already been used in semiconductor devices, wireless communications, telecommunications, integrated circuits, rectifiers, transistors, solar cells, light-emitting diodes, photoconductors, light crystal displays, magneto-optic memories, audio and video systems, compact discs, electro-optic coatings, memories, multilayer capacitors, flat-panel displays, smart windows, computer chips, magneto optic discs, lithography, micro electromechanical systems (MEMS), and multifunctional emerging coatings, as well as other emerging cutting technologies.

i) Optical Coatings:

An optical coating is one or more thin layers of material deposited on an optical component such as a lens or mirror, which alters the way in which the optic reflects and transmits light. One type of optical coating is an antireflection coating, which reduces unwanted reflections from surfaces, and is commonly used on spectacle and photographic lenses. Another type is the high-reflector

coating which can be used to produce mirrors which reflect greater than 99.99% of the light which falls on them. More complex optical coatings exhibit high reflection over some range of wavelengths, and anti-reflection over another range, allowing the production of dichroic thin-film optical filters.

ii) Photovoltaic:

In the familiar rigid solar panel, the energy of incoming photons is converted to electricity in cells containing two thin layers of crystalline silicon. What makes roll-to-roll production of flexible film solar products possible is replacement of the crystalline silicon with amorphous silicon, supplied in high-solids slurries that can be deposited onto substrates by web-converting processes like slot die coating. Micro layer film, EDI can outfit its Contour cast film dies with a new system, based on technology licensed from 'The Dow Chemical Company', which makes it possible to produce film of standard thickness, yet with dozens of exceedingly thin 'micro-layers'. The multiple layer-to-layer interfaces create a torturous path for gas molecules and thus substantially increase the barrier properties of the film. This is critical for photovoltaic applications, which require barrier layers to prevent performance losses caused by infiltration of oxygen or moisture vapor. In working with solar product manufacturers, EDI draws on extensive experience in other applications that require thin-gauge, optically clear, close-tolerance films and coatings with critical functionalities, including films and coatings for flat panel displays and flexible batteries particularly relevant, since solar cells are a kind of battery. In comparison with conventional coating methods, such as spray, roll, and spin coating, slot dies provide greater control over coating weight and distribution because they are closed systems into which coating material is pumped at closely pre-determined rates; in turn this greater control makes possible thinner coatings," Many in the solar power industry and the investment community, believe the arrival of grid parity, the point when cost of electricity generated by a rooftop photovoltaic (PV) cell system is equivalent to that purchased from an electrical utility will mark a major inflection point for the market that will deliver a huge increase in growth. However, even when true grid parity arrives, it's unlikely to generate an abrupt rise in solar system installations due to the high upfront costs and the long-term return of investing in a rooftop photovoltaic system

iii) Semiconductor:

Historically, the semiconductor industry has relied on flat, two-dimensional chips upon which to grow and etch the thin films of material that become electronic circuits for computers and other electronic devices. This thin layer (only a couple of hundred nanometers thick) can be transferred to glass, plastic or other flexible materials, opening a wide range of possibilities for flexible electronics. In addition, the semiconductor film can be flipped as it is transferred to its new substrate, making its other side available for more components. This doubles the possible number of devices that can be placed on the film. By repeating the process, layers of double-sided, thin film semiconductors can be stacked together, creating powerful, low-power, three dimensional electronic devices. "It's important to note that these are single-crystal films of strained silicon or silicon germanium. The strain is introduced in the way we form the membrane. Introducing strain changes the arrangement of atoms in the crystal such that we can achieve much faster device speed while consuming less power." For non-computer applications, flexible electronics are beginning to have significant impact. Solar cells, smart cards, radio frequency identification (RFID) tags, medical applications, and active-matrix flat panel displays could all benefit from the development. The techniques could allow flexible semiconductors to be embedded in fabric to create wearable electronics or computer monitors that roll up like a window shade. "This is potentially a paradigm shift. The ability to create fast, low-power, multilayer electronics has many exciting applications. Silicon germanium membranes are particularly interesting. Germanium has a much higher adsorption for light than silicon. By including the germanium without destroying the quality of the material, we can achieve devices with two to three orders of magnitude more sensitivity." That increased sensitivity could be applied to create superior low-light cameras, or smaller cameras with greater resolution.

iv) Photo Electrochemical Cells (PEC):

In photo electrochemical experiments, irradiation of an electrode with light that is absorbed by the electrode material causes the production of a current (a photocurrent). The dependence of the photocurrent on wavelength, electrode potential, and solution composition provides information about the nature of the photo process, its energetic, and its kinetics. Photocurrents at electrodes can also arise because of photolytic processes occurring in the solution near the electrode surface. Photo electrochemical studies are frequently carried out to obtain a better understanding

of the nature of the electrode-solution interface. Photo electrochemistry and Electro generated Chemiluminescence photocurrent can represent the conversion of light energy to electrical and chemical energy; such processes are also investigated for their potential practical applications. Since most of the studied photo electrochemical reactions occur at semiconductor electrodes.Consideration of semiconductor electrodes also helps in gaining a microscopic understanding of electron-transfer processes at solid-solution interfaces.

v) Optoelectronic:

An optoelectronic thin-film chip, comprising at least one radiation-emitting region in an active zone of a thin-film layer and a lens disposed downstream of the radiation emitting region, said lens being formed by at least one partial region of the thin-film layer, the lateral extent of the lens being greater than the lateral extent of the radiation emitting region. The thin-film layer is provided for example by a layer sequence which is deposited epitaxially on a growth substrate and from which the growth substrate is at least partly removed. That is to say that the thickness of the substrate is reduced. In other words, the substrate is thinned. It is furthermore possible for the entire growth substrate to be removed from the thin-film layer. The thin-film layer has at least one active zone suitable for generating electromagnetic radiation. The active zone may be provided for example by a layer or layer sequence which has a PN junction, a double hetero structure, a single quantum well structure or a multiple quantum well structure. Particularly preferably, the active zone has at least one radiation-emitting region. In this case, the radiation-emitting region is formed for example by a partial region of the active zone. Electromagnetic radiation is generated in said partial region of the active zone during operation of the optoelectronic thin-film chip.

vi) Flat Panel Displays:

Developed from the Mykrolis contamination control technologies, Entegris provides a broad portfolio of liquid and gas contamination control technologies for the flat panel display fabrication. The Flat Panel Display (FPD) fabrication environment is among the worlds most competitive and technologically complex. Device designers and manufacturers continually strive to satisfy the worldwide consumer’s appetite for larger displays, greater pixel resolution and

feature-rich performance – all at a lower cost than the previous generation of technology. The need to control contamination in air, gas and liquid process streams is now a paramount focus of process engineers and designers.

vii) Data Storage:

As the data storage density in cutting edge microelectronic devices continues to increase, the superparamagnetic effect poses a problem for magnetic data storage media. One strategy for overcoming this obstacle is the use of thermomechanical data storage technology. In this approach, data is written by a nanoscale mechanical probe as an indentation on a surface, read by a transducer built into the probe, and then erased by the application of heat. An example of such a device is the IBM millipede, which uses a polymer thin film as the data storage medium. It is also possible, however, to use other kinds of media for thermomechanical data storage, and in the following work, we explore the possibility of using thin film Ni-Ti shape memory alloy (SMA). Nanometer-scale indentations made in martensite phase Ni-Ti SMA thin films recover substantially upon heating. Issues such as repeated thermomechanical cycling of indentations, indent proximity, and film thickness impact the practicability of this technique. While there are still problems to be solved, the experimental evidence and theoretical predictions show SMA thin films are an appropriate medium for thermomechanical data storage.

viii) Super Capacitor:

Since first patents were in the 1950, the idea of storing charge in the electric double layer that founds at the interface between a solid and an electrolyte has presented itself as an attractive notation while was considerable development was carried out by the slander oil company, Cleveland, Ohio (SOHIO) in the 1960 a lack of sales lead them to license the technology to Nippon electric company. The first high power double layer capacitor were developed for military applications by the pinnacle research institute in 1982. Conventional capacitor stores energy electrostatically on two electrode separated by a dielectric, the capacitance of which is C= €A/d, where € being the dielectric constant, A surface area and d the dielectric thickness. In a double layer capacitor, charges accumulate at the boundary between electrode and electrolyte to form two charge layers with separation of several Angstroms. Super capacitors are electrochemical energy storage device. The away that super capacitor store energy is based in

principal on two type's capacitive behavior the electrical double layer capacitance from the pure electrostatic charge accumulation at the electrode interface and the pseudo-capacitance developed from fast and reversible surface redox process at characteristic potential. Super capacitor integrated in to hybrid vehicle, power source, power control, multi source supply, fuel save etc.

ix) Gas Sensors:

Advancements in micro technology and the evolution of new nonmaterial and devices have been playing a key role in the development of very accurate and reliable sensors. The technology of sensors has developed tremendously in the last few years owning many scientific achievements from various experiments, offering newer challenges and opportunity to the quest for every smaller devices capable of molecular level imaging and monitoring of pathological samples and the macromolecules has lately gained the focus of attention of the scientific community, particularly for remote monitoring due to the increasing need for environmental safety and health monitoring. Gas sensors generally operate different principles and various gas sensing elements have been developed have been past years, out of which resistive metal oxide sensors comprise a significant part. However these sensing elements typically operate at an elevated temperature for maximum performance. This makes higher power consumption which is not suitable for the inflation. Over the last decayed carbon nanotube has attracted considerable attention, and great efforts have been made to exploit their unusual electronic and mechanical properties. These properties make them potential candidates for building blocks of active materials in nanoelectronics, field emission devices, gas storage and gas sensors. Among these the room temperature gas sensing property is very attractive for many applications.

4. Methodology to be adopted:

Among the available wide organic and Inorganic materials some of the materials have found growing interest among researchers in recent years, In this current proposal, the researchers investigate in detail specific broad categories of novel material systems that have caught the intense research interest among the community, internationally. The electrode and gas-phase phenomena in various kinds of glow discharges (especially RF discharges) represent a rich source of processes used to deposit and etch thin films. Chemical reactions are accelerated at a given temperature in the presence of energetic reactive-ion bombardment is the basis of processes for surface treatments such as plasma oxidation, plasma nitridation, and plasma carburizing. Plasma deposition of inorganic films and plasma polymerization of organic reactants to produce films of organic polymers involve the introduction of a volatile reactant into a glow discharge which is usually generated by an RF force. ECR plasma Deposition employs an electron cyclotron resonance (ECR) ion source to create high-density plasma. The plasma is generated by resonance of microwaves and electrons through a microwave discharge across a magnetic field. Film formation by purely chemical processes in the gas or vapor phases includes chemical vapor deposition and thermal oxidation. Chemical vapor deposition (CVD) is a materials synthesis process whereby constituents of the vapor phase react chemically near or on a substrate surface to form a solid product. The selection of a specific technology for the deposition of thin films can be based on a variety of considerations. A multitude of thin films of different materials can be deposited for a large variety of applications; hence, no general guidelines can be given of what the most suitable deposition technology should be. In selecting an appropriate deposition technology for a specific application, several criteria have to be considered. The desired material characteristics of the deposited films will be, in most cases, the decisive factor for the selection of a preferred deposition technology.

5. Importance of study/ Society application:

Moore's law, which predicts the exponential increase in the number of transistors integrated on a single chip. The increased performance of the devices is the consequence of improvements in both architecture and physical scaling of the devices. In every logic circuit, the key element is the metal–oxide–semiconductor (MOS) transistor, which basically constitutes an electrical switch. The scaling of MOSFET was easily accomplished using SiO_2 as gate oxide layer but fundamental limit is the exponential increase of direct tunneling current as function of the SiO_2 thickness. The concept of High-K replace is quite simple in principle. In order to reduce direct tunneling, make the physical thickness of the gate dielectric larger, but keep the capacitance the same as an equivalent SiO_2 film. 'High−K' gate oxide materials such as Al_2O_3, ZrO_2, HfO_2, Ta_2O_5, TiO_2, Er_2O_3, La_2O_3, Pr_2O_3, Gd_2O_3, Y_2O_3, CeO_2 etc. and some of their silicates such as $Zr_xSi_{1-x}O_y$, $Hf_xSi_{1-x}O_y$ and $Al_xZr_{1-x}O_2$ etc. are under investigation.

Thin film solar cells are favorable because of their minimum material usage and rising efficiencies. The three major thin film solar cell technologies include amorphous silicon (α-Si), Copper Indium Gallium Selenide (CIGS), and Cadmium Telluride (CdTe). Recent trends suggest that few perovskite oxides ABO_3, $A_2BB'O_6$, $A_2A'B_2B'O_9$ are under investigation.

Gas sensors are used for fire detection, detection of gas in different spaces, i.e. in transportation of sensitive materials. Marine and navy applications are therefore very important. Metal oxide semiconductor gas sensors are utilised in a variety of different roles and industries. They are relatively inexpensive compared to other sensing technologies, robust, lightweight, long lasting and benefit from high material sensitivity and quick response times. They have been used extensively to measure and monitor trace amounts of environmentally important gases such as carbon monoxide and nitrogen dioxide.

6. Proposed work Plan/ Formulation and Structure of Study:

- Fabrication Method depending upon application
- Cleaning of substrate
- Selecting best materials depending on application followed by deposition method
- Optimisation of process parameter e.g. Vacuum pressure, Subject to target distance, deposition time, film thickness etc.....
- Selection and Deposition of metal contact
- Fabrication steps photolithography, etching etc....
- Select best characterisation method.
- Simulation of result by COMSOL,SCAPS or Coventorware simulator.

Thin films can be characterized many different ways, for any given thin film we are normally only interested in three or four crucial properties. These important properties will vary from application to application. The most common thin film properties and their associated measurement techniques are listed below,

* Thickness (spectrophotometer, ellipsometer, step height, Electron microscope, RBS, quartz crystal monitor).

* Optical properties: refractive index, extinction coefficient, transmission, reflection, absorption (spectrophotometer, ellipsometer).

* Electrical (4 point probe, eddy current, C-V and I-V measurement).

* Crystal structure (TEM, XRD), Microstructure (SEM).

* Chemical/Elemental Composition (AES, XPS, EDAX, SIMS).

* Thin film stress (Curvature of coated sample). Thin film adhesion (Tape test, pull tester).

References:

1. High-k perovskite gate oxide BaHfO3 Young Mo Kim, Chulkwon Park, Taewoo Ha APL materials Jan 2017.
2. High-K materials and metal gates for CMOS applications John Robertson, Robert M.Wallace Sciencedirect(Material science and engineering) Feb 2015.
3. Fabrication of high-k dielectric Calcium CopperTitanate (CCTO) target by solid state route, N Tripathy,K C Das, S P Ghosh, G Bose, J P Kar (Material science and engineering) 2016
4. High dielectric constant oxides J. Robertson Appl. Phys. 28, 265–291 (2004)
5. Fabrication and characterization of metal–semiconductor–metal ultraviolet photodetector based on rutile TiO2 nanorod Abbas M. Selman, Z. Hassana Materials Research Bulletin 73 (2016)
6. MOS technology: challenges for future decelopment,B.scilicic Journal of Maritime Studies Vol 20,No 2(2006) pp 97-104.
7. Preparation and gas-sensing properties of perovskite-type SrFeO oxide Yude Wang, Jingbo Chen, Xinghui Wu Materials Letters 49 Ž2001.361–364
8. High-k dielectrics for future generation memory devices J.A. Kittl a, K. Opsomer, M. Popovici Microelectronic Engineering 86 (2009) 1789–1795
9. Chemical sensors based on a high-k perovskite oxide of barium strontium titanate C. Hucka, A. Poghossiana Procedia Engineering 87 (2014) 28 – 31
10. Perovskite oxides for semiconductor-based gas sensors Jeffrey W. Fergus Sensors and Actuators B 123 (2007) 1169–1179
11. Screen-printed perovskite-type thick films as gas sensors for environmental monitoring Giuliano Martinelli, Maria Cristina Carotta Sensors and Actuators B 55 (1999) 99–110
12. Physicochemical properties of rare earth perovskite oxides used as gas sensor material Tsuyoshi Arakawa, Hiroshi Kurachi Ournal Of Materials Science 20 (1985) 1207-1210

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